

A Novel Desulfurizer-Catalyst Combination for Logistic Fuel Reforming

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Editor's Note: Many different approaches will be required to provide the warfighter with a full spectrum of power and energy solutions. One of the more promising of these is fuel cell technology. However, some of the major hurdles for fuel cells to clear include developing suitable hydrogen-rich fuels to sustain them and being able to produce these fuels in both an efficient and environmentally-friendly manner. This article is a summary of leading edge research in the development of new catalytic materials to enhance the production of the needed fuels. This state-of-the-art work was performed by Dr. Abdul-Majeed Azad and his graduate student Desikan Sundararajan of the University of Toledo. If you are interested in learning more about this technology or would like to contact the authors, please contact the AMMTIAC Editor.

INTRODUCTION

The emerging generation of high efficiency fuel cells will require clean power sources that are readily and reliably available. The best sources at present to meet that need are the vast reserves of logistic fuels (jet fuels, diesel, and coal) available to the Department of Defense (DoD). However, each of these fuel sources must be converted into hydrogen-rich streams through a chemical reformation process. Unfortunately, each of these fuel sources contains unacceptable levels of sulfur mostly as organosulfur. Upon combustion, the sulfur is typically combined with elements in the reaction to form one of several molecules, such as hydrogen sulfide (H_2S), sulfur dioxide (SO_2) or sulfur trioxide (SO_3). These are atmospheric pollutants which can be deleterious to air quality and some of which may also lead to acid rain in certain regions of the country.

Thus, it is necessary to remove any sulfur species from these logistic fuels during the reforming process. Chemical reformers in fuel production are typically catalytic vessels. For instance, these reactors contain a bed of a noble metal, usually platinum, that serves as a catalyst* to drive the conversion reaction of the fuel. Unfortunately, a conventional reformer would be hindered by the presence of sulfur in these fuels, as sulfur poisons or renders the catalyst inactive.

The best way to overcome these challenges would be to develop a new generation of effective desulfurizer and sulfur-tolerant reforming catalysts. Meeting these two objectives, specifically an agile desulfurizer capable of sorbing sulfur in the fuel and a sulfur-tolerant catalyst that can tolerate the brunt of a small level of sulfur left uncaptured by the sulfur sorbent, calls for innovative approaches. The research summarized in this article highlights the feasibility of generating clean electric power using desulfurized hydrogen-rich reformates from logistic fuels with reduced environmental impact.

APPLICATION

The immediate applications for hydrogen-powered fuel cells are many: military field operations, including mobile forward base units, auxiliary field hospitals, field command posts, operational

forays, unmanned aerial vehicle flights, and aircraft auxiliary power units (APUs) would all benefit from the extended capabilities this type of technology would provide. By extension, this process could be applied beyond refined petroleum fuels to gasified coal-based fuel cell systems. This latter concept could extend the adaptation of fuel cell-based power systems to reach an even broader user segment: the public sector.

The DoD is the largest single user of petroleum products in the world, comprising nearly two percent of total US fuel consumption. The cost of crude oil, amounting to \$12.6 billion in 2007, represents a substantial transfer of tax revenue to foreign countries, several of which are adversarial to the United States' strategic interests. Both of these factors, specifically the volume of fuel consumption as well as the sources for some of these fuels, would dictate more efficient use of fuel resources and the synthesis of alternative fuels.

In the light of eventual energy shortages, the ever-increasing global demand for fuel, and the quest for cleaner and greener energy, there is great interest in using logistic fuels. The use of hydrogen-rich reformates of logistic fuels, such as JP-5, JP-8, or Jet-A, are attractive as feeds for polymer electrolyte membrane fuel cells (PEMFCs) and solid oxide fuel cells (SOFCs) for NASA and the Army. NASA envisions employing fuel cells running on clean reformat from jet fuels in their future unmanned aerial vehicles (UAVs) and low emission alternate power (LEAP) missions, as well as transcontinental flights[1, 2, 3]. However, depending on the source and kind, jet and other logistic fuels are invariably sulfur-laden; the sulfur content in them varies between 0.3 to more than 1 weight percent (wt%), hence the need to develop robust sulfur-tolerant catalysts to facilitate the continuous uninterrupted operation of logistic fuel processors.

APPROACH

One major alternate source of transportation fuel is gasification of virtually any gaseous, liquid, or solid hydrocarbon into a liquid fuel. Yet most fuel synthesis processes are based on the gasification of fossil fuels, which produce a variety of undesirable "greenhouse" gases. So even in the development of alternative fuels,

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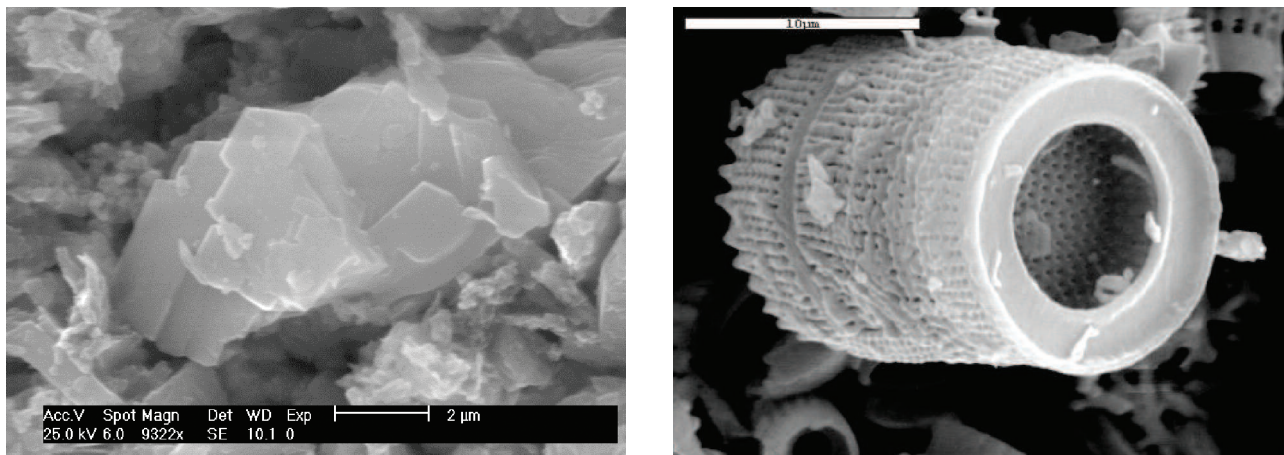


Figure 1. SEM images of clinoptilolite (left) and diatomite (right) support matrix.

there is the looming emphasis on reducing the production of greenhouse gases. The efforts to reduce carbon dioxide emissions in the way energy is produced and used may represent one of the more important technological developments of the 21st century.

The general approach in this effort was to fabricate and evaluate a series of desulfurizers based on a lightweight nanoporous matrix, embedded with agile sulfur-binding species to facilitate sulfur absorption. Designing an intelligent composite between the sorbent material and the sulfur-tolerant nanocatalyst creates a realistic combination of properties to achieve these goals, which an energy supplier/end-user would find appealing.

This research examined the performance of nanoscale, ceria-supported, sulfur-tolerant catalysts with nominal loading of noble metals (NM, total NM ≤ 1 wt%; NM = mono-, bi- or tri-metal dispersion). These formulations were assessed in terms of their sulfur-tolerance, phase integrity and the quality of reformat using kerosene (JP-8 surrogate), at temperatures typically employed in reforming. Some salient features of novel, low-cost, lightweight desulfurizers were assessed in terms of their sulfur capture under conditions of high sulfur exposure at temperatures

typically employed in reforming. Since the final chemical state of sulfur species in the fuel reformat is H_2S [4], desulfurization studies were carried out using streams containing 1000 and 3000 parts per million (ppm) H_2S in the range at 600-800°C for soak-time up to 350h.

Desulfurizers

The first step was to find a suitable support material to host the sorbent. Diatomaceous earth and clinoptilolite (zeolitic clay) were used as inert support materials for synthesizing the sulfur sorbents. Scanning electron microscope (SEM) micrographs of these materials are shown in Figure 1. The sorbents were made by dispersing selected metal oxides onto the support materials.

The adsorption performance of each combination of the desulfurizing material was evaluated by exposing the sorbent in powder form to a H_2S -laden stream of nitrogen for several hours at several test temperatures. The absorbency of each material was evaluated by measuring the H_2S concentration in the exit stream using a gas chromatograph.

It was found that the sulfur capture propensity of these formu-

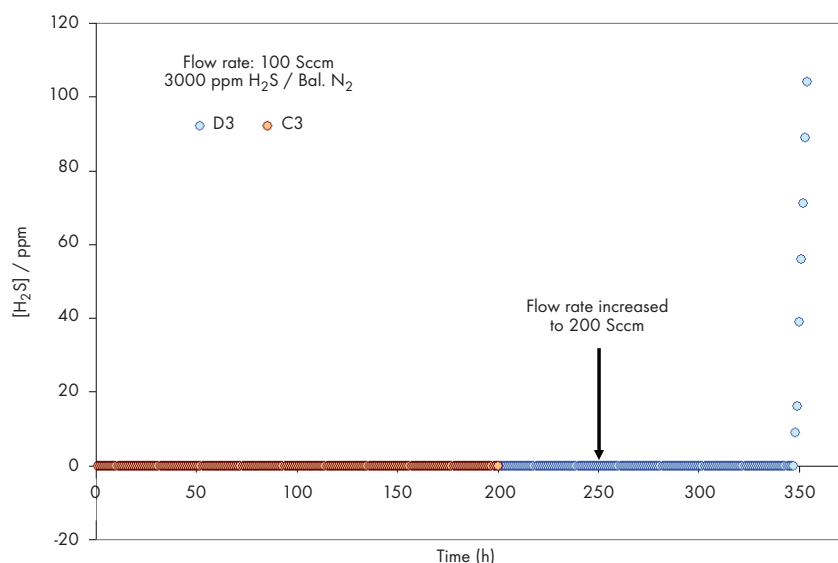


Figure 2. Sulfur capture by the sorbents in long-term tests at 800°C.

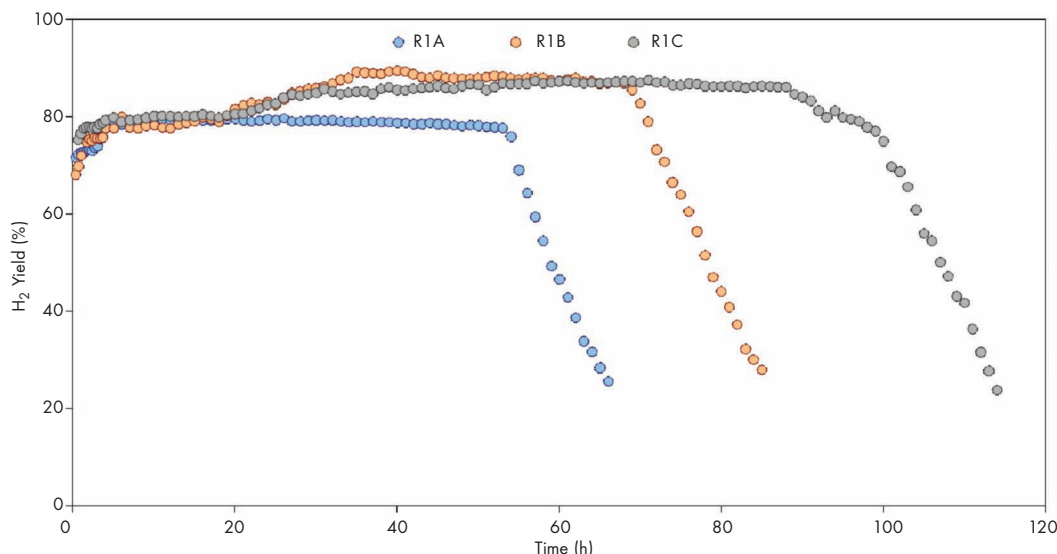


Figure 3. Catalytic performance measured in terms of hydrogen yield by three different catalysts.

lations increases with increase in temperature. Thus, in the range of 500-800°C, the best results were obtained at 800°C. The sulfur capture capacity increases considerably upon coating the desulfurizer on 1 x 9 inch corrugated stainless steel foils to enhance the surface area.

The time dependence of sulfur capture by the clinoptilolite-based (C-series) and diatomite-based (D-series) sorbents on the foils during long-term (approximately 350h) exposure to a stream containing 3000 ppm H₂S is shown in Figure 2. As can be seen, no breakthrough (in terms of sulfur signal shown by the flame photometric detector (FPD) of the GC) was observed with either sorbent, up to 200h on stream. In order to induce breakthrough, the flow rate was doubled after 250h on stream in the case of D3. Saturation of the sorbent sets in after the 347th hour on stream, as can be seen from the rise in H₂S signal in GC at the end of this period.

Sulfur-Tolerant Reforming Catalysts

Catalysts were made by dispersing noble metals onto the ten mole percent gadolinia-doped ceria (GDC) support material. The catalysts were characterized by a host of analytical techniques with respect to their structural, morphological, chemical and thermal qualities. The performance of three catalysts was evaluated by measuring the hydrogen yield from the steam reforming of kerosene at 800°C. A sample graph is shown in Figure 3.

Since these reformates originate from kerosene that contains 260 ppm of sulfur, it is important to study the difference in performance of these three catalysts in terms of their sulfur tolerance. For this purpose, the sulfur levels in the exit stream was also followed online during the reforming experiments. The concentration of H₂S as a function of the progress of the reaction is shown in Figure 4.

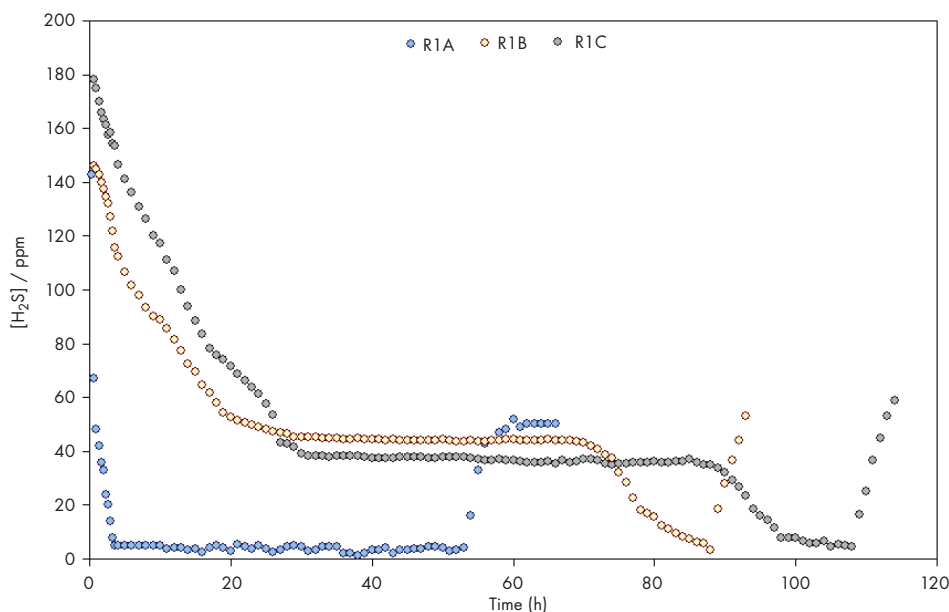


Figure 4. Trend in H₂S concentration in the exit stream with different catalysts.

The stability trend with respect to sulfur tolerance observed in Figure 4 is complimentary to that seen in Figure 3 in terms of hydrogen yield. For example, the sulfur level (in terms of H_2S) drops rather quickly in the early stage of reformation, during which the hydrogen yield is somewhat lower, signifying that a steady-state has not yet been reached. Beyond this, the concentration of sulfur is somewhat constant; this is seen as the active phase of the catalyst where the hydrogen yield is stable and high for an extended period. Once the active noble metal sites get completely sulfided, deactivation via sulfur poisoning ensues and the hydrogen yield begins to decrease.

SUMMARY

The initial results yielded from this study were very encouraging: nanoscale-doped-ceria proved a good candidate support material in the development of novel sulfur-tolerant catalyst formulations. It was found that all formulations evaluated exhibited sulfur-tolerance without significant reduction in active surface area (a measure of catalytic performance). Steam-reforming experiments with kerosene (JP-8 surrogate) yielded a reformat rich in hydrogen and significantly reduced sulfur content. Several desulfurizer formulations were synthesized on clinoptilolite and diatomaceous earth support matrices, which showed excellent performance at various temperatures between 500 and 800°C. The results of this study would suggest that a combina-

tion of an agile desulfurizer formulation with an optimal sulfur-tolerant nanocatalyst would provide an ideal combination to obtain a ready-to-use, sulfur-free, hydrogen-rich feed for SOFCs from a variety of logistic fuels.

NOTE & REFERENCES

* A *catalyst* is a material that, when present, will facilitate or in most cases accelerate the reaction rate of the chemical species in a reactor. A catalyst is not a reactant and thus is not consumed in the reaction. Catalysts work because their surfaces attract the various reactant molecules, which then combine more easily by their proximity to one another on the surface. Once the reaction is completed, the product molecule typically releases from the catalyst. In an automobile's catalytic converter, for example, the unconsumed hydrocarbons, carbon monoxide and nitrogen oxides in the exhaust are allowed to run over a noble metal (platinum or palladium) catalyzed monolithic bed, which instantly converts these species into carbon dioxide, water and nitrogen molecules.

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Dr. Abdul-Majeed Azad is an Associate Professor in the Department of Chemical Engineering at the University of Toledo; he has been serving the university in this capacity since August '03. Dr. Azad began his career as a Research Scientist studying fast breeder nuclear reactor materials with a special focus on their processing and characterization aspects. His current interests are in the area of nanomaterials, including metals, functional ceramics and composites. Dr. Azad is particularly interested in the relevance of nanomaterials to clean energy, catalysis, sensors, biomedical applications and other nanotechnologies.

Mr. Desikan Sundararajan is a doctoral student in the Department of Chemical Engineering at the University of Toledo, with a research focus on the development of sulfur tolerant nanocatalysts and desulfurizers for logistic fuel reforming. He received an MS in Environmental Engineering from the University of Arizona and a BS in Chemical Engineering from the University of Pune, India. He will receive his PhD in the summer of 2009.